

# Self-consistent Green function approach for calculations of electronic structure in transition metals

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## Abstract

We present an approach for self-consistent calculations of the many-body Green function in transition metals. The distinguishing feature of our approach is the use of the one-site approximation and the self-consistent quasiparticle wave function basis set, obtained from the solution of the Schrodinger equation with a nonlocal potential. We analyze several sets of skeleton diagrams as generating functionals for the Green function self-energy, including GW and fluctuating exchange sets. Their relative contribution to the electronic structure in 3d-metals was identified. Calculations for Fe and Ni revealed stronger energy dependence of the effective interaction and self-energy of the d-electrons near the Fermi level compared to s and p electron states. Reasonable agreement with experimental results is obtained.

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Density-functional theory (DFT), in particular the local-density approximation (LDA), has proven to be a rather successful *ab-initio* approach to describe physical properties of many materials. Nevertheless numerous applications of this method have revealed a number of shortcomings related to the inadequate treatment of both excited (energy gap) and strongly correlated states. For a long time the many-body Green function (GF) approach was considered as a possible *ab-initio* alternative to DFT, but its current applicability is usually restricted to the homogeneous electron gas (HEG) model[1, 2, 3] or semiconductors in the GW approximation. However, realization of the full self-consistent GW scheme is complicated due to enormous computational difficulties. As a result, for the transition metals (TM) the GW approach was applied only to Ni[4, 5] and these calculations used the wave functions obtained within the LDA as the basis set, i.e. they were not self-consistent. Thus, it is quite unlikely that a universal GF method can be formulated and tailoring the approximations to specific properties of a given class of materials is desirable. The localized character of the d-wave function in TM often implies the well-known one-site approximation[6] which in real systems acquires certain material specific features.

Already the calculations of Refs.[4, 5] revealed a strong energy-dependence of the effective interaction in TM, even in the vicinity of the Fermi level. For example in Ni the effective Coulomb interaction  $W$  is nearly zero at 6 eV and increases to an unscreened value of 20-25 eV at 20 eV. Another important observation is related to a proper intra-atomic scale treatment. Elementary analysis shows that the  $d$ -function in bcc Fe is significantly altered at a distance as small as 0.8 a.u., while  $s$  and  $p$  wave functions are altered at distances of about the Wigner-Seitz radius ( $\sim 2.6$  a.u.). The “local” screening length,  $\lambda = \kappa^{-1}$  ( $\kappa^2(r) = 4\pi e^2 \Pi_0(\rho(r))$ , with  $\Pi_0(\rho(r)) = (3/\pi\rho)^{1/3}/\pi$ ), which varies from 0.5 a.u. in the region of the maximum of the  $d$ -wave function to a value of 1.0 a.u. at the atomic sphere (AS) boundary, provides an initial justification for the one-site approximation and suggests that the correct material-specific implementation must include a spatially resolved representation of the polarization operator (PO) and other two-channel operators, at least inside the AS. We believe that the energy dependence and intra-atomic resolution are both crucial for the quantitative description of TM and must be included explicitly in any reliable technique. On the other hand, we will show below that this approximation can describe the essential physics of TM, greatly reducing the computational efforts.

In the present paper we incorporate the effects described above into the self-consistent

GF technique using the quasiparticle wave function basis set and the Luttinger-Ward functional[7] (LWF) approach for the self-energy calculations. We tested several sets of diagrams, mainly from the fluctuating-exchange subset (FLEX)[8]. All diagrams beyond these sets were taken in the local approximation. The use of the LWF guarantees the equivalence of one-particle properties calculated with the GF and with the corresponding total energy variation[9]. The LWF formalism naturally leads to the integration over the imaginary axis, greatly improving the numerical accuracy of the integration. On the imaginary axis both the GF and PO quickly reach their quasiclassical limits, are sufficiently smooth, and are determined by the local potential only[10]. The rotation of the integration contour leads to a very convenient separation of the structural and local density dependent degrees of freedom for both self-energy and total energy[11, 12]. Also, in contrast with the numerical method[3] we analytically select the contributions from both the GF cut on the real axis and the integration along the imaginary axis. An energy linearization of the quasiparticle wave function similar to the one in linear density functional methods was used.

In terms of an exact GF the thermodynamic potential is written as[7]

$$\Omega = -Tr \{ \ln [\Sigma - G_0^{-1}] \} - Tr \Sigma G - \Phi \quad (1)$$

where  $\Sigma$  is the self-energy,  $G$  and  $G_0$  are exact and 'bare' GF and  $\Phi$  is the Luttinger generating functional, which is represented by the set of skeleton graphs. Minimizing  $\Omega$  over  $G$  one can obtain[7]

$$\Sigma = \frac{\delta \Phi}{\delta G} \quad (2)$$

The expressions for  $\Phi$  for the most important two-particle (hole) channels are summarized in Ref.8. The set from Fig.1b with 'bare' loops corresponds to the GW-approximation. After variation of  $\Phi$  over the GF, which we consider as a variational variable, one can obtain the usual GW expression for the self-energy:

$$\Sigma(\varepsilon) = - \int G(\varepsilon - \omega) V_c \Pi(\omega) W(\omega) \frac{d\omega}{2\pi i} \quad (3)$$

where  $V_c$  is the Coulomb interaction and  $W$  is the effective interaction  $W = V_c / (1 + V_c \Pi)$ . It is convenient to rotate the contour of integration in Eq.(3) in the complex plane, using the fact that  $\Pi(z)$  has no singularities in the first and third quadrants[13, 14], whereas  $G$  has a singularity (cut) in the third quadrant for  $\varepsilon < E_F$  and in the first one for  $\varepsilon > E_F$ . In the case of the quasiparticle the singularities of the GF are simple poles. After rotation the

only additional contribution comes from the cut of the GF (Fig 1e), and for  $\varepsilon < E_F$  this contribution is

$$\Sigma_{ca}^p = \int_{\varepsilon}^0 g(\omega') \Pi(\varepsilon - \omega') V_c W(\varepsilon - \omega') d\omega' \quad \varepsilon < 0,$$

where  $g(\omega) = -\text{Im } G(\omega) \text{sgn} \omega / \pi$ . For the term corresponding to the integration along the imaginary axis we obtain

$$\Sigma_{ca}^i = \int_{-\infty}^{\infty} d\omega' \int_0^{\infty} \frac{d\omega}{2\pi i} g(\omega') \frac{2(\varepsilon - \omega')}{(\varepsilon - \omega')^2 + \omega^2} \Pi(i\omega) V_c W(i\omega)$$

At  $E_F$ ,  $\varepsilon = 0$  and the pole term disappears. The term  $\Sigma_{ca}^i$  is usually negative in the HEG model. On the real axis  $\Pi(\omega)$  has an imaginary part, which is important for accurate calculations of  $W(\omega)$  in TM. The summation over  $\mathbf{k}$  (one-site approximation) transforms all the above formulas into matrix equations on the local wave function basis, greatly reducing the computational efforts. The full on-site GF  $G(\mathbf{r}, \mathbf{r}', \varepsilon) = \sum_{\mathbf{k}} (G_0^{-1}(\mathbf{r}, \mathbf{r}', \varepsilon, \mathbf{k}) - \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon))^{-1}$  was obtained self-consistently from Eq.(3). Due to the large value of  $\partial \Sigma / \partial \varepsilon$  in TM, the final  $G$  differs significantly from the initial  $G_0$ . The quantity  $\Pi(\mathbf{r}, \mathbf{r}', \varepsilon) = \int G(\varepsilon) G(\varepsilon + \omega) d\varepsilon / 2\pi i$  was also obtained self-consistently with the full  $G$ .

Let us discuss the choice of skeleton graphs for the LWF. According to perturbation theory with Coulomb parameter  $\alpha = e^2 m / p_f$  the exchange diagram (Fig 1a) gives the largest contribution. The set of empty bubble diagrams (Fig.1b) gives the next term  $\alpha^2 \ln 1/\alpha$ . The summation of these terms is necessary to take into account the long-distance character of the Coulomb interaction. In addition, the proper treatment of the "dressed" GF in the bubble approximation must include vertex corrections[15] (Fig.1b). The next term (Fig.1c) is just the exchange diagram in the second-order approximation, which has an order of  $\alpha^2$ . It can be important in magnets, as the corresponding self-energy depends only on the GF with the same spin, while in bubble diagrams both spins are averaged. In principle, the Fig.1c diagram is already included in the set, if the bubble diagrams with vertex corrections are considered. But it seems desirable to include also the ladder sequence of Fig.1d, as it is also highly spin dependent. This set does not contain the first ( $\alpha^2$ ) term[8]. Such a sum is reduced by the effective screening of the Coulomb potential, which in turn strongly depends on the energy. The static value of the effective interaction is rather small, but it quickly increases as a function of energy (Fig.2b). We evaluated this sum of lattice-type T-matrix diagrams (Fig.1d) with the effective interaction replacing the energy dependent potential

by the averaged static interaction  $\zeta V_c$ . The parameter  $\zeta$  was chosen in such a way that the value of the diagrams on Fig.1c obtained with both energy dependent and  $\zeta V_c$  type of interactions were the same. The value of  $\zeta$  turned out to be  $\sim 0.35$ .

The diagrams discussed above are also the leading diagrams from the point of view of the one-site approximation. The number of d-electrons with various angular moment projections  $m_z$  is approximately the same in both Ni and Fe. If we take into account that the main contribution in the Coulomb interaction, expanded in spherical harmonics  $V(\mathbf{r} - \mathbf{r}') = \sum_L Y_L(\hat{r})Y_L(\hat{r}')(r_{<}/r_{>})^l$  is from the term with  $l = 0$ , then, with this accuracy,  $m_z$  is conserved and one can classify various diagrams with the parameter  $1/N = 1/(2l+1)$ . For d electrons this is a small parameter and the main terms with  $1/N$  are again FLEX diagrams[16]. In summary, we believe, that the set of diagrams in Fig.1 is the minimal set which must be included in the calculations. On the other hand, our calculations revealed that it can be sufficient for description of magnetic properties and electronic structure of 3d metals.

The rotation of the integration contour allows us to deal only with the states lying in the vicinity of  $E_F$ [12], as the PO is smooth and decreases when  $\text{Im } \varepsilon$  is increased, contrary to its behavior on the real axis. This is shown in Fig.2a,b for ferromagnetic Fe. For the states near  $E_F$  we can use the GF constructed with low lying LMTO states  $\Psi_{\mathbf{k}}^\nu(\mathbf{r}) = \sum_L a_{\mathbf{k}}^{\nu\alpha} \phi_l^\alpha(r) Y_L(\hat{n})$ , where  $\phi_l^0(r)$  and  $\phi_l^1(r)$  are the corresponding solutions of equations

$$\hat{G}_{0l}^{-1} \phi_l^0(r) = (\varepsilon - \hat{T}) \phi_l^0(r) - \int V(\mathbf{r}, \mathbf{r}') \phi_l^0(r') d^3 r' = 0 \quad (4)$$

$$\hat{G}_{0l}^{-1} \phi_l^1(r) = -\phi_l^0(r) - \int \frac{\partial \Sigma(\varepsilon_l, \mathbf{r}, \mathbf{r}')}{\partial \varepsilon_l} \phi_l^0(r') d^3 r', \quad (5)$$

with  $V(\mathbf{r}, \mathbf{r}') = \Sigma(\varepsilon_l, \mathbf{r}, \mathbf{r}')$ .  $\varepsilon_l$  is the center of gravity of the band with orbital moment  $l$  and  $a_{\mathbf{k}}^{\nu 0}$  are the eigenvectors of the generalized eigenvalue problem with the Hamiltonian

$$H = H_0 + \Sigma_l(\varepsilon) - \Sigma_l(\varepsilon_l) - (\varepsilon - \varepsilon_l) \dot{\Sigma}_l(\varepsilon_l) \quad (6)$$

which is a matrix in the space of LMTO states  $\phi + h\dot{\phi}$ , where  $h_{LL'}$  are the usual LMTO coefficients. This procedure takes into account the energy-independent exchange potential  $\Sigma_x = 1/2\pi i \int V_c \text{Im} G d\varepsilon$  exactly.

The important problem in the nonlocal calculations is the inclusion of the valence-core interaction. In our method we included the core-valence exchange term exactly, whereas

the core-valence correlation term was added using the approximation developed in Ref.[17]. The latter term in TM such as Fe, Ni or Cu is small. The set of Eqs.(4),(5) was solved iteratively[12]. The integral equation for the screened interaction  $D(\omega, \mathbf{r}, \mathbf{r}')$  was solved using the product basis introduced in Ref.[18].

The procedure above was applied to the 3d transition metals Fe and Ni. The main contribution to the self-energy comes from the exchange diagram (Fig 1a), but the pure exchange approximation produces too large a self-consistent magnetic moment  $M$  ( $M \sim 3.05\mu_B$  in Fe (see also Ref.[19] )). The bubble diagrams screen the Coulomb interaction, either too strongly ( $M \sim 1.95\mu_B$  in Fe) or too weakly ( $M \sim 0.73\mu_B$  in Ni). Vertex corrections only slightly modify this result, uniformly reducing the interaction for both spins. The conclusions in general agree with GW results for the HEG[1, 2, 3], though the importance of the exchange T-matrix diagram (Fig 1d) is rather intrinsic to TM[8, 20]. With all considered diagrams the calculated equilibrium magnetic moments ( $2.04\mu_B$  in Fe and  $0.65\mu_B$  in Ni ) are close to LDA values ( $2.15\mu_B$ ,  $0.62\mu_B$ ) and experimental values ( $2.08\mu_B$ ,  $0.59\mu_B$ ).

The GF calculations naturally provide valuable information about the renormalization and damping of the electron spectra which are absent in LDA. In Fig.3 we present the energy dependence of the real ( $\Sigma^R$ ) and imaginary ( $\Sigma^I$ ) parts of the self-energy  $\Sigma_{2a}$ .  $\Sigma^R(\omega)$  is linear in a wide range of energies, supporting the concept of well-defined quasiparticles. On the other hand the renormalization factor  $Z_l = 1/(1 - \partial\Sigma/\partial\varepsilon)$  strongly depends on the orbital number  $l$ . For  $s$  and  $p$  electrons  $Z_l$  is about 0.96 and is in good agreement with the HEG estimations ( $Z \sim 1 - 0.04e^2m/p_f$  [13]). But for  $d$  electrons this factor is about 0.6 in Ni and 0.7 in Fe, pointing out severe many-body effects. The value  $Z_d$  was calculated self-consistently and in Ni it approximately coincides with the value calculated with a non-self-consistent (using LDA wave functions) method[4].

Previous studies revealed that the most significant differences between the LDA and experimental results are the satellite peak below the quasiparticle band (approximately 6-8 eV below  $E_F$ ) and a larger value of the density of states (DOS) at the Fermi level  $N(E_F)$ . As a result, the overall experimental bandwidth (7-8 eV in Fe and 6-7 eV in Ni) is larger than what is found in the LDA along with the larger values of  $N(E_F)$ . Extracted from the linear term in the heat capacity, the experimental DOS values are 57 st/a.u. in Fe and 81 st/a.u. in Ni. Though a considerable amount of this value can be ascribed to the electron-phonon interaction, they are still much larger than the ‘bare’ LDA values in Fe (30 st/a.u.) and in

Ni (48 st/a.u.).

The small value of  $Z_d$  obtained above leads to a narrowing of the quasiparticle band. The rest of the one-electron states take part in the formation of the satellite structure, which usually appears when the hole-hole interaction is taken into account[20]. Consequently our DOS (Fig.4) is also wider compared to the LDA DOS and has a bump below the quasiparticle DOS. The value of the DOS at the Fermi level is even lower than in the LDA, though the value of coefficient  $\gamma$ , which is  $1/Z$  times larger than the DOS, is approximately the same as in LDA. Both values are still lower than the experimental values. It can be due to the high sensitivity of the Stoner splitting in ferromagnets (and in turn the value of  $N(E_F)$ ) to all the approximations used or possible narrowing of the hopping between neighboring sites in the spirit of the Gutzwiller approximation or the Dynamical Mean Field Theory, which is omitted in our approximation.

In conclusion, we have proposed a new self-consistent version of the GF approach, which uses the quasiparticle wave functions as a basis set. We found that self-consistent GW approach produces the leading contribution to the electronic structure and magnetic properties of TM, whereas the addition of fluctuating exchange diagrams overall slightly corrects this result improving comparison with experiment. While the self-consistent renormalization factors  $Z_l$  for  $s$  and  $p$  electrons in Ni and Fe are close to the estimations obtained from the HEG,  $Z_d$  is much smaller (0.6-0.7). The values of bandwidth and density of states at the Fermi level are in reasonable agreement with experiment. The proposed technique can be naturally used for total energy calculations. In summary we believe that the proposed technique can be considered as a practical *ab-initio* alternative to modern DFT methods with much wider range of applicability.

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## FIGURE CAPTIONS

Fig 1 The diagram representation of: (a) exchange energy, (b) "bubble" set with vertex corrections for the polarization operator, (c) exchange diagram of second order (d) exchange T-matrix set. The integration contour and pole positions in the complex energy plane are shown in (e).

Fig 2. The energy dependence of the real and imaginary parts of the polarization operator

with  $l = 2$  on the real axis (a). The same for the polarization operator and effective interaction  $V_{eff} = \sum_l D_l Z_l / Z$  on the imaginary axis (b).

Fig 3. The energy dependence of the partial components of self-energy in ferromagnetic Fe: (a) the real part and (b) absolute value of imaginary part.

Fig 4. The density of states in bcc Fe for the majority (solid) and minority (dashed) spin states.







